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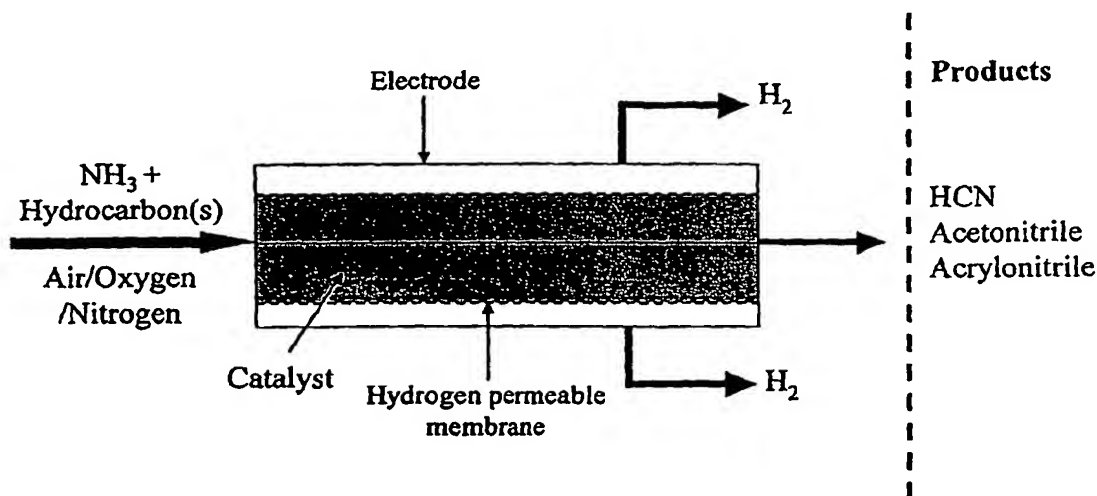
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(54) Title: SYSTEM AND METHOD FOR THE MANUFACTURE OF HYDROGEN CYANIDE AND ACRYLONITRILE WITH
SIMULTANEOUS RECOVERY OF HYDROGEN



(57) Abstract: A system and method for the manufacture of hydrogen cyanide, acrylonitrile, and acetonitrile are provided. The system comprises at least one pulsed corona discharge reactor with each pulsed corona discharge reactor having a reaction zone. At least one reactant feed stream containing hydrogen is introduced into the pulsed corona discharge reactor and contacting the catalyst wherein hydrogen is removed from the reactant to form hydrogen cyanide, acrylonitrile, and acetonitrile.



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SYSTEM AND METHOD FOR THE MANUFACTURE OF HYDROGEN
CYANIDE AND ACRYLONITRILE WITH SIMULTANEOUS RECOVERY OF
HYDROGEN

The present application is a continuation and claims priority of pending provisional patent application Serial No. 60/411,816, filed on September 18, 2003, entitled "System and Method for the Manufacture of Hydrogen Cyanide and Acrylonitrile with Simultaneous Recovery of Hydrogen".

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to system and method for the manufacture of hydrogen cyanide and acrylonitrile and, more particularly, the invention relates to system and method for the manufacture of hydrogen cyanide and acrylonitrile with simultaneous recovery of hydrogen in a pulsed corona discharge reactor.

2. Description of the Prior Art

Hydrogen cyanide is used for the production of chemical intermediates employed in the manufacture of nylon acrylic sheetings and coatings (methyl methacrylate), gold mining chemicals, animal feed supplements, water treatment, agricultural chemicals and herbicides, pharmaceuticals, household products, chelating products, among others. The annual production of cyanide (as HCN) actually exceeds 1.25 million metric tons per annum. Though several processes are available for the manufacture of HCN, the most popular are:

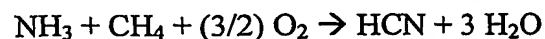
• **Shawnigan process:**

The following reaction is employed:



• **Andrussow process:**

This process, widely used for the manufacture of HCN, involves the use of the autothermal reactions of ammonia, methane and air over a platinum and rhodium gauze catalyst. The overall reaction can be represented as



A variant, with the addition of a lower amount of oxygen, leads to the formation of both hydrogen and water. Thus,



2 • **BMA process:**



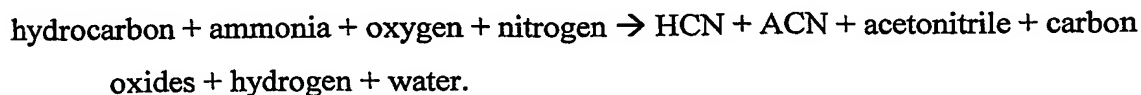
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5 HCN can also be produced as a by-product in the manufacture of acrylonitrile
6 (ACN, $\text{CH}_2=\text{CHCN}$) using the SOHIO process for the ammoxidation of propylene
7 and ammonia. Air, ammonia and propylene are reacted in the presence of catalyst at 5
8 – 30 psig, and temperatures of 1000 °F. Approximately, 1.5 billion pounds of ACN
9 are produced each year in the U.S. alone. The major use is in the production of acrylic
10 and modacrylic fibers – these fibers are marketed under the trade names Acrilan,
11 Creslan, Verel, among others. Other uses include manufacture of acrylonitrile-
12 butadiene-styrene (ABS) and styrene-acrylonitrile (SAN) resins, nitrile elastomers,
13 and other chemicals. Acrylonitrile is also used as a fumigant.

14 In all these processes, as also noted earlier, platinum and rhodium based
15 catalysts are necessary; in addition, high-temperature operation is required. The
16 controlled addition of oxygen (air) provides the heat necessary for the reaction, and
17 also permits regeneration of the catalyst.

18
19 SUMMARY

20 The present invention is a system for the manufacture of hydrogen cyanide,
21 acrylonitrile, and acetonitrile. The system comprises at least one pulsed corona
22 discharge reactor with each pulsed corona discharge reactor having a reaction zone.
23 At least one reactant feed stream containing hydrogen is introduced into the pulsed
24 corona discharge reactor and contacting the catalyst wherein hydrogen is removed
25 from the reactant to form hydrogen cyanide, acrylonitrile, and acetonitrile.

26 In addition, the present invention includes a system for the manufacture of
27 hydrogen cyanide, acrylonitrile, and acetonitrile. The system comprises a pulsed
28 corona discharge reactor and a feed stream introduced into the pulsed corona
29 discharge reactor wherein the following reaction is created:



1 The present invention further includes a method for manufacturing hydrogen
2 cyanide, acrylonitrile, and acetonitrile. The method comprises providing at least one
3 pulsed corona discharge reactor with each pulsed corona discharge reactor having a
4 reaction zone, positioning a catalyst in the reaction zone, introducing at least one
5 reactant feed stream containing hydrogen into the pulsed corona discharge reactor and
6 contacting the catalyst, and removing hydrogen from the reactant to form hydrogen
7 cyanide, acrylonitrile, and acetonitrile.

8 9 BRIEF DESCRIPTION OF THE DRAWINGS

10 FIG. 1a is a schematic view illustrating a system and method, constructed in
11 accordance with the present invention, wherein hydrocarbon and ammonia are the
12 reactants;

13 FIG. 1b is a schematic view illustrating a system and method, constructed in
14 accordance with the present invention, with the inclusion of a suitable solid phase
15 catalyst within the reaction zone;

16 FIG. 1c is a schematic view illustrating a system and method, constructed in
17 accordance with the present invention, with air, oxygen, and/or nitrogen being
18 introduced;

19 FIG. 1d is a schematic view illustrating a system and method, constructed in
20 accordance with the present invention, with a feed stream similar to FIG. 1c, but with
21 use of a suitable solid phase catalyst in the reaction zone; and

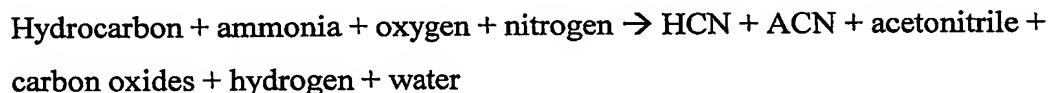
22 FIG. 1e is a schematic view illustrating a system and method, constructed in
23 accordance with the present invention, with hydrocarbon and ammonia being fed into
24 separate discharge reactors for generation of the appropriate radicals.

25 26 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

27 Hydrogen cyanide and acrylonitrile are important chemical intermediates used
28 in a variety of applications of importance in the chemical, pharmaceutical, and mining
29 industry. The present invention is a system and method for the manufacture of
30 hydrogen cyanide and acrylonitrile, in particular, as well as acetonitrile. The reactants
31 – ammonia, and hydrocarbons, for example, methane – are brought into contact in a
32 single or plurality of pulsed corona or silent barrier discharge reactor(s). The reaction
33 zone within the discharge reactor may contain suitable catalyst. Air, oxygen and/or

1 other combinations of nitrogen and oxygen may be added to the feed stream
2 depending on the product stream desired. The walls of the reactor are preferably
3 constructed from membrane materials suitable for the selective continuous removal of
4 hydrogen – formed from the decomposition of the ammonia and hydrocarbon(s) –
5 from the reaction zone. Continuous removal of hydrogen from the reaction zone
6 drives the reaction toward completion, and provides an important product stream.

7 As described above, the system and method of the present invention is the
8 manufacture of HCN and acrylonitrile, in particular, as well as acetonitrile. The
9 reactants – ammonia, and hydrocarbons, for example, methane – are brought into
10 contact in a single or plurality of pulsed corona or silent barrier discharge reactor(s).
11 The reaction zone within the discharge reactor may contain suitable a catalyst. Air,
12 oxygen and/or other combinations of nitrogen and oxygen may be added to the feed
13 stream depending on the product stream desired. Inert gases, for example, argon
14 and/or helium may be added also to increase the density of ions in the reaction zone.
15 Thus,



20 Hydrocarbon species used would depend on the final product requirement – examples
21 include methane, ethane, propane, propylene, and ethylene, among others.

22 Pulsed corona and silent barrier discharge systems do not appear to have been
23 used for these reactions. In these reactors, a non-thermal plasma is formed in the
24 reaction zone, and the reactions of interest are facilitated. Examples of the use of
25 these reactors for other applications – notably in the area of NO_x destruction, and the
26 treatment of hydrogen sulfide – have been reported. Note that non-equilibrium, or
27 non-thermal, plasmas have been divided into five distinctive groups depending on the
28 mechanism used for their generation, applicable pressure range, and electrode
29 geometry. These are as follows:

- 30
31 • *Glow discharge*: This is an essentially low-pressure phenomenon usually between
32 flat electrodes. The low pressure and mass flow severely restrict chemical
33 industrial application.

- 1 • *Corona Discharge*: Use of inhomogeneous electrode geometries permits
2 stabilization of discharges at high pressure. Several specific regions of operation –
3 for example, ac or dc, and pulsed – have been described in the literature for
4 applications involving, most often, cleanup of flue gas and atmospheric pollutants.
5 The *AC/DC* corona discharges, however, are inefficient in their higher energy
6 consumption.
- 7 • *Silent Discharge*: In this operational regime, one or both of the electrodes are
8 covered with a dielectric layer. Application of a sinusoidal (or other time-varying)
9 voltage, then, leads to pulsing electric fields and micro-discharges similar to those
10 observed in pulsed corona discharge systems.
- 11 • *RF Discharge*: In such systems, the electrodes are not an integral part of the
12 discharge volume. Non-thermal (or non-equilibrium) conditions are expected only
13 at low pressures, whereas thermal or equilibrium plasmas can be expected at high
14 pressures – and larger production rates – of interest in the chemical process
15 industry.
- 16 • *Microwave Discharge*: Here, similar to RF discharge systems, the electrodes are
17 not an integral part of the discharge volume. The wavelength of the applied
18 electromagnetic field becomes comparable to the dimensions of the discharge
19 volume and necessitates other coupling mechanisms.

20

21 In comparing these non-thermal plasmas, it must be noted that in a glow discharge,
22 the electrons gain energy from the applied field. Due to low pressures, collision with
23 neutral species is infrequent. Propensity for the creation of reactive ions and chemical
24 species is limited. Steady state operation is governed, primarily, by loss of energy
25 incurred by the electrons on enclosure walls and other surfaces within the reactor.
26 The situation is similar in RF and microwave discharges. In corona and silent
27 discharges, the situation is *entirely* different – the fast electrons do indeed transfer
28 energy to other molecules in the system. Electrode geometry and construction prevent
29 sparking or arcing. The collision between electrons and the molecules leads to the
30 production of ions and reactive species that facilitates chemical reaction at ostensibly
31 low temperatures. The pulsing of the corona discharge permits significant reduction
32 in the power consumption.

1 Another distinguishing feature of the proposed process is the use of pulsed
2 corona and silent barrier discharge reactors that permit selective removal of hydrogen
3 from the reaction zone. Many reactions of importance in the process and petroleum
4 industry are limited by thermodynamic constraints on (closed system) equilibrium
5 conversion. In such reactions, the reactant conversion can often be enhanced by use
6 of membrane reactors that operate on the principle of continuous / intermittent
7 removal of products from the reaction zone. A particularly important category of such
8 reactors is that based on the use of (catalytic, or non-catalytic) reactors membranes
9 that are selective to the permeation of hydrogen. This configuration permits
10 overcoming the equilibrium conversion limitations, and provides a relatively pure
11 stream of hydrogen that may be

- 12 • recycled to the refinery for use in hydrogenation applications; and / or
- 13 • used as a clean fuel – in a fuel cell, or in direct combustion applications.

14 For example, an inventor of the present application has described the use of pulsed
15 corona and silent barrier discharge reactors for the decomposition of H_2S ; the reactor
16 walls, constructed from hydrogen-permeable membrane materials remove hydrogen
17 from the reaction zone and serve simultaneously as an electrode. High voltage pulses,
18 with duration of about tens of nanoseconds, create an intense electric field most in the
19 reaction zone leading to the formation of a non-thermal plasma. The temperature of
20 the electrons formed from the ionization of the gaseous medium, as characterized by
21 electron velocity / energy, is much higher than the temperature of the much larger bulk
22 gas molecules and other ionic/charged/excited species.

23 Examples of possible configurations are illustrated in FIG. 1. In FIG. 1a, a
24 hydrocarbon and ammonia are the reactants. FIG. 1b illustrates the inclusion of a
25 suitable solid phase catalyst within the reaction zone. In FIG. 1c, the addition air,
26 oxygen, and/or nitrogen is shown; FIG. 1d illustrates a similar feed stream but with
27 use of a suitable solid phase catalyst in the reaction zone. In FIG. 1e, the hydrocarbon
28 and ammonia are fed into separate discharge reactors for generation of the appropriate
29 radicals; these radicals are combined, in the presence of a suitable solid phase catalyst
30 if necessary, in a separate reaction chamber. Air, oxygen and/or nitrogen may be
31 added in these reactors. Other combination(s) of such reactors are also possible.

32 The major advantages of the proposed process are as follows:

- 1 • The operation can be carried out at low temperatures with or without the use of
2 expensive catalyst.
- 3 • The reactor operation can be brought on-line, or shut off, through
4 instantaneous control of electrical current and voltage, which adds a large
5 margin of safety to production of this toxic material. Expensive and extensive
6 clean-up procedures following shutdown, necessary in the conventional
7 catalytic high-temperature operation, are rendered unnecessary.
- 8 • Removal of hydrogen from the reaction zone permits recovery of a valuable
9 commodity. It also permits driving the reaction towards completion.
- 10 • The product mix can be controlled readily.

11

12 Reactant conversion or product yield can often be enhanced by use of
13 membrane reactors that operate on the principle of continuous/intermittent removal of
14 products from the reaction zone. An important category of such reactors is that based
15 on the use of membranes that are selective to the permeation of hydrogen. In the
16 present invention, a system and method is described for the characterization of
17 hydrogen-permeable membranes. The system and method of the present invention
18 will, in particular, find application where the permeability of hydrogen has to be
19 measured for membranes to be used in reactors that employ electrical/electrochemical/
20 photo-electrochemical fields that lead to generation of hydrogen.

21

22 The foregoing exemplary descriptions and the illustrative preferred
23 embodiments of the present invention have been explained in the drawings and
24 described in detail, with varying modifications and alternative embodiments being
25 taught. While the invention has been so shown, described and illustrated, it should be
26 understood by those skilled in the art that equivalent changes in form and detail may
27 be made therein without departing from the true spirit and scope of the invention, and
28 that the scope of the present invention is to be limited only to the claims except as
29 precluded by the prior art. Moreover, the invention as disclosed herein, may be
30 suitably practiced in the absence of the specific elements which are disclosed herein.

31

1

1 CLAIMS

2

3 What is claimed is:

4

5 1. A system for the manufacture of hydrogen cyanide, acrylonitrile, and
6 acetonitrile, the system comprising:
7 at least one pulsed corona discharge reactor, each pulsed corona discharge
8 reactor having a reaction zone; and
9 at least one product stream containing hydrogen produced in the pulsed corona
10 discharge reactor and contacting the catalyst;
11 wherein hydrogen is removed from the reactant to form hydrogen cyanide,
12 acrylonitrile, and acetonitrile.

13

14 2. The system of claim 1 wherein the pulsed corona discharge reactor has walls,
15 the walls being constructed from membrane materials suitable for the selective
16 continuous removal of hydrogen formed from the decomposition of the ammonia and
17 hydrocarbon(s) in the reaction zone wherein the continuous removal of hydrogen from
18 the reaction zone drives the reaction to completion.

19

20 3. The system of claim 1 wherein the reactant feed stream has an additive
21 selected from the group consisting of air, oxygen and other combinations of nitrogen
22 and oxygen.

23

24 4. The system of claim 1 wherein the reactant feed stream includes ammonia and
25 hydrocarbons.

26

27 5. The system of claim 4 wherein the hydrocarbons include methane, ethane,
28 propane, propylene, and ethylene.

29

30 6. The system of claim 1 and further comprising:
31 inert gases added to the reaction zone for increasing the density of ions in the
32 reaction zone.

1

2 7. The system of claim 1 wherein the pulsed corona discharge reactor operates on
3 continuous/intermittent removal of products from the reaction zone.

4

5 8. The system of claim 1 and wherein the reactants are hydrocarbon and
6 ammonia, a solid phase catalyst is positioned within the reaction zone, and air,
7 oxygen, and/or nitrogen are added to the feed stream.

8

9 9. The system of claim 1 wherein the reaction zone contains a catalyst.

10

11 10. A system for the manufacture of hydrogen cyanide, acrylonitrile, and
12 acetonitrile, the system comprising:

13 a pulsed corona discharge reactor; and

14 a feed stream introduced into the pulsed corona discharge reactor;

15 wherein the following reaction is created:

16 hydrocarbon + ammonia + oxygen + nitrogen \rightarrow HCN + ACN + acetonitrile +
17 carbon oxides + hydrogen + water.

18

19 11. A method for manufacturing hydrogen cyanide, acrylonitrile, and acetonitrile,
20 the method comprising:

21 providing at least one pulsed corona discharge reactor, each pulsed corona
22 discharge reactor having a reaction zone;

23 positioning a catalyst in the reaction zone;

24 introducing at least one reactant feed stream containing hydrogen into the
25 pulsed corona discharge reactor and contacting the catalyst; and

26 removing hydrogen from the reactant to form hydrogen cyanide, acrylonitrile,
27 and acetonitrile.

28

29 12. The method of claim 11 and further comprising:

30 constructing the walls of the pulsed corona discharge reactor has walls from
31 membrane materials suitable for the selective continuous removal of
32 hydrogen formed from the decomposition of the ammonia and

1 hydrocarbon(s) in the reaction zone wherein the continuous removal of
2 hydrogen from the reaction zone drives the reaction to completion.

3

4 13. The method of claim 11 and further comprising:
5 introducing an additive selected from the group consisting of air, oxygen and
6 other combinations of nitrogen and oxygen into the reactant feed
7 stream.

8

9 14. The method of claim 11 and further comprising:
10 adding ammonia and hydrocarbons into the reactant feed streams.

11

12 15. The method of claim 14 wherein the hydrocarbons include methane, ethane,
13 propane, propylene, and ethylene.

14

15 16. The method of claim 11 and further comprising:
16 increasing the density of ions in the reaction zone with inert gases added to the
17 reaction zone.

18

19 17. The method of claim 11 and further comprising:
20 operating the pulsed corona discharge reactor on continuous/intermittent
21 removal of products from the reaction zone.

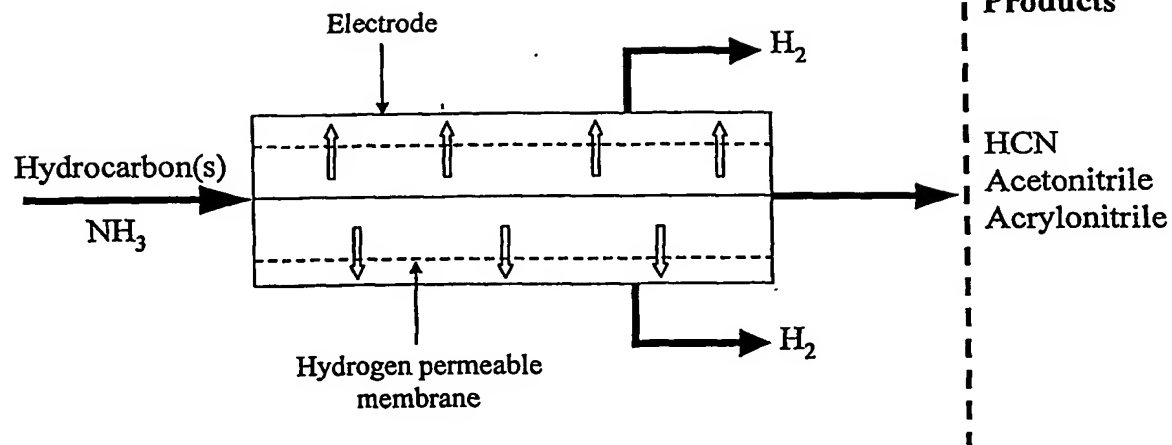
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23 18. The method of claim 11 and wherein the reactants are hydrocarbon and
24 ammonia, a solid phase catalyst is positioned within the reaction zone, and air,
25 oxygen, and/or nitrogen are added to the feed stream.

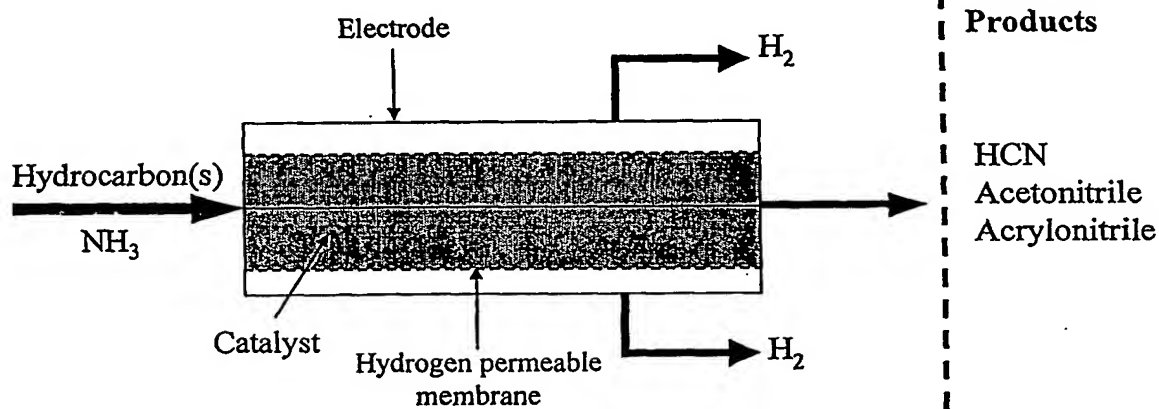
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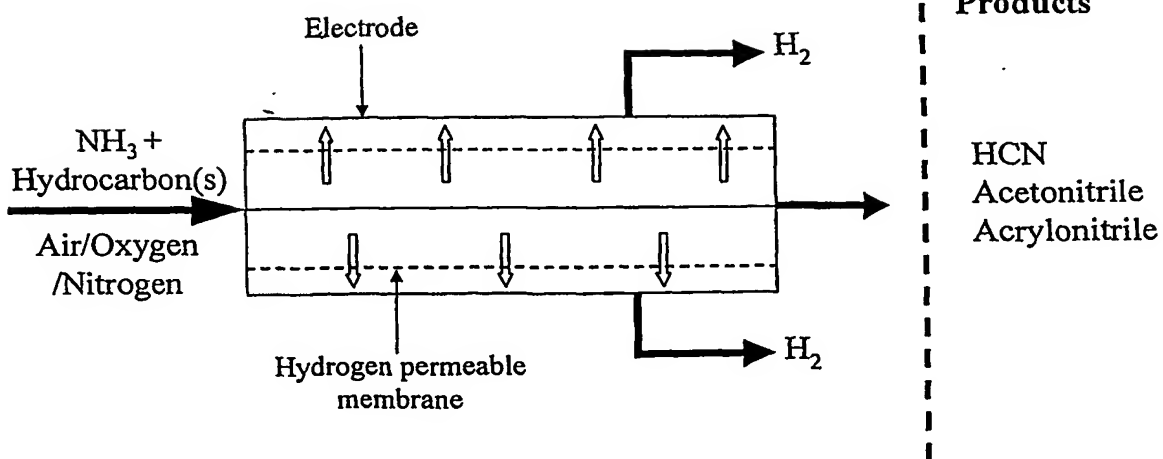
1a)



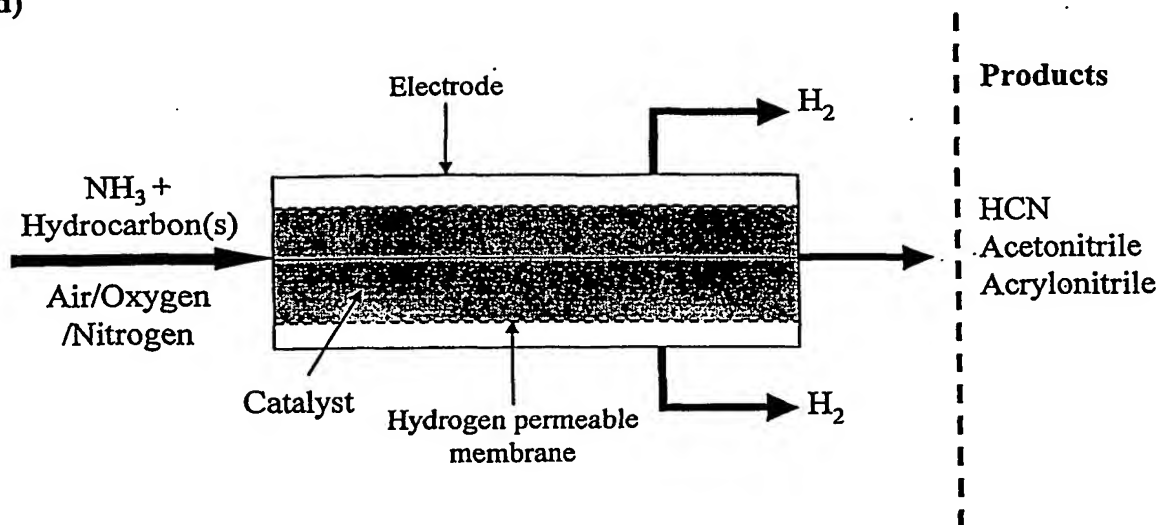
1b)



1c)



1d)



1e)

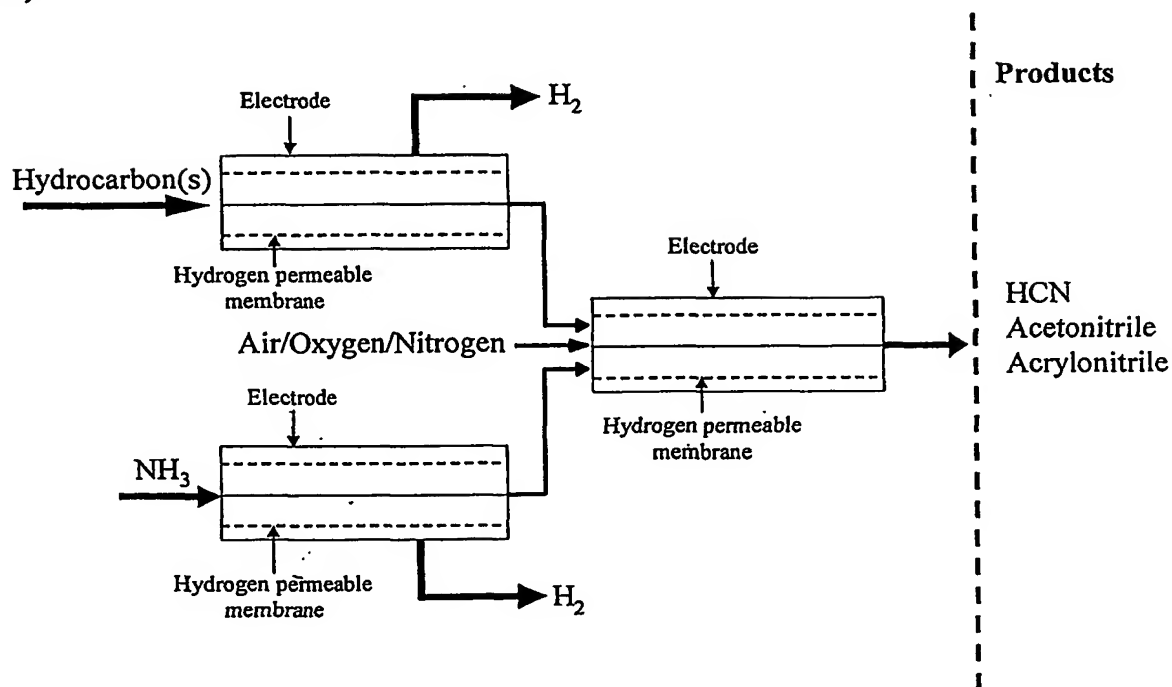


Figure 1: Typical reactor configurations for the synthesis of HCN and ACN

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/29419

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B01J 19/08

US CL : 422/186.04; 204/164,165

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 422/186.04; 204/164,165

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WEST; CAPLUS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6,096,173 A (VON HIPPEL et al.) 1 August 2000, see abstract; col. 2, line 66 through col. 3, line 10; col. 3, lines 53-54; col. 1, lines 9-20 and col. 1, line 59 through col. 2, line 2.	1-18
X	US 6,245,309 B1 (ETIEVANT et al.) 12 June 2001, see abstract.	2, 12

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

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